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Application of electric field to increase effectiveness of penetrating corrosion inhibitors for steel in concrete

1. Introduction

Corrosion of reinforcing steel is considered as a main factor responsible for the deterioration of functional parameters of reinforced concrete structures and repairs of damaged structures are troublesome and very expensive. Increasing the durability of concrete constructions is currently a civilization challenge. Corrosion inhibitors are one of protection methods against steel corrosion in concrete (1, 2). Penetrating corrosion inhibitors (PCIs), also called MCIs, or surface applied inhibitors, are able to penetrate through concrete to steel and reduce its corrosion. They can be easy applied on concrete surface by spray or brush. PCIs effectively inhibit the corrosion process, if their concentration near the reinforcement is sufficiently high. The main limitation of the use of PCIs is their slow transport in concrete. The effective diffusion coefficients for these inhibitors are similar or even less as compared to value for chloride ions (3). To increase the inhibitors effectiveness, methods for the acceleration of their transport in concrete should be developed. A few such approaches are postulated, first of all: the vacuum-pressure method (4, 5) and electrochemical injection (6-13). The vacuum-pressure method, consisting in the vacuum removal of moisture from concrete and then the application of inhibitor under pressure, is very complicated and costly for real constructions. The electrochemical injection consists in the acceleration of inhibitors transport upon an impressed electric field. This approach seems to be easier to implement on a concrete construction as compared to the vacuum-pressure method.

The electric field affects the transport of charged species, and therefore, the application of the electrochemical injection is possible only for inhibitors that are present in form of ions. In the literature, only a few papers are devoted to the problem of electrochemical injection of corrosion inhibitors into concrete. They mainly concern amine derivatives, which are mostly used as PCIs. Under proper conditions, an amine molecule can undergo protonation (bonding with H^+ ion) and form positively charged ion. Such ionic derivatives of amines can be transported in electric field, to cathodically polarized steel rebar (6-9). However, the protonation of amines proceeds at pH range characteristic for the individual amine and, for many amines of interest, this reaction is effective at pH values

much less than those typical for pore solution of sound concrete. For instance, the penetration of ethanolamine was enhanced by the application of electric field in carbonated concrete, but not in noncarbonated one (6-8). The electric field induced transport of phosphonium corrosion inhibitors (quaternary phosphonium cations: $(C_2H_5)_4P^+$, $(C_4H_9)_4P^+$, $(C_6H_5)_4P^+$) in concrete was also studied, but the effect in terms of transfer numbers was slight (10-11, 13). Calcium nitrite is one of the most effective corrosion inhibitors for steel in concrete (1, 14). This compound is present in concrete pore solution in dissociated form and nitrite anions, NO_2^-, are responsible for the inhibitive action. This satisfies the fundamental criterion for the possibility of electrochemical injection. However, there is a scarce information about the acceleration of concrete penetration by nitrite ions. The ingress of these anions into concrete was accelerated by the electric field between two external electrodes, located on the opposite sites of mortar sample (12). The published studies of the electrochemical injection of corrosion inhibitors into concrete are far from systematic.

The purpose of this study was to determine the effect of the electric field on the transport rate of nitrite ions in mortar. Measurements were performed in mortar samples of varying degree of carbonation and chloride contamination, to evaluate the role of mortar features.

2. Experimental

Experiments were performed in a two-chamber set-up with mortar membrane (Fig. 1). The inhibitor (calcium nitrite) was present in one chamber (cathodic) and, under the influence of an electric field, nitrite ions migrated through mortar membrane to second (anodic) chamber. The initial concentration of nitrite ions in the cathodic chamber was 1 mol/dm³. The anodic chamber was filled with saturated solution of calcium hydroxide with a significant excess of undissolved $Ca(OH)_2$ (14 g $Ca(OH)_2$ was added to 1250 g water). The mortar membranes were made of Portland cement OPC I 32.5 R, river sand and tap water. The membranes were characterized by water to cement ratio = 0.7 and cement to aggregates ratio = 0.25. The thickness of membrane was 2.5 cm, and its surface area in contact with the solution was 81 cm². A stainless

steel plate with surface area of about 180 cm² was used as the cathode, while five graphite rods with a total surface area of 230 cm² served as the anode. Some membranes were contaminated with chloride ions (1% of Cl⁻ by weight of cement). Moreover, some of chloride non-contaminated and contaminated membranes were carbonated to determine the influence of chloride ions and carbonation on the electrochemical injection. Electric current intensity between 1 to 40 mA, which corresponds to 0.1-4.9 A/m² of mortar surface, was applied to the tested systems for 7 days. Reference tests without electric field, where the inhibitor diffused driven only by the concentration difference, were also conducted for the all studied membranes. Voltage between the electrodes, the inhibitor concentration and the pH of the solutions in both chambers were measured during the tests. The nitrite concentration in the cathodic chamber was determined by UV spectrophotometry, whereas in the anodic chamber (to which inhibitor migrated and its concentration was low) the Griess method (15) was used. The carbonation degree of membranes was found out by tests with phenolphthalein and thymolphthalein. Absorbabilities of mortar membranes were determined according to the procedure described in the Polish standard PN-B-06250:1988 (16). Most experiments were performed at least twice to prove the reproducibility.
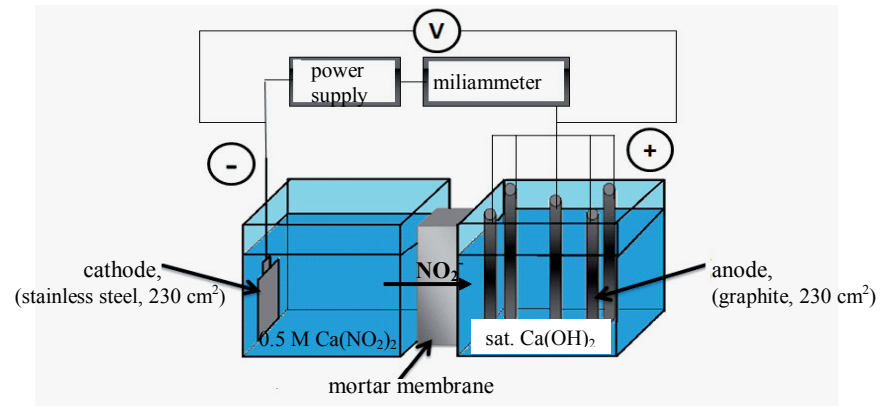

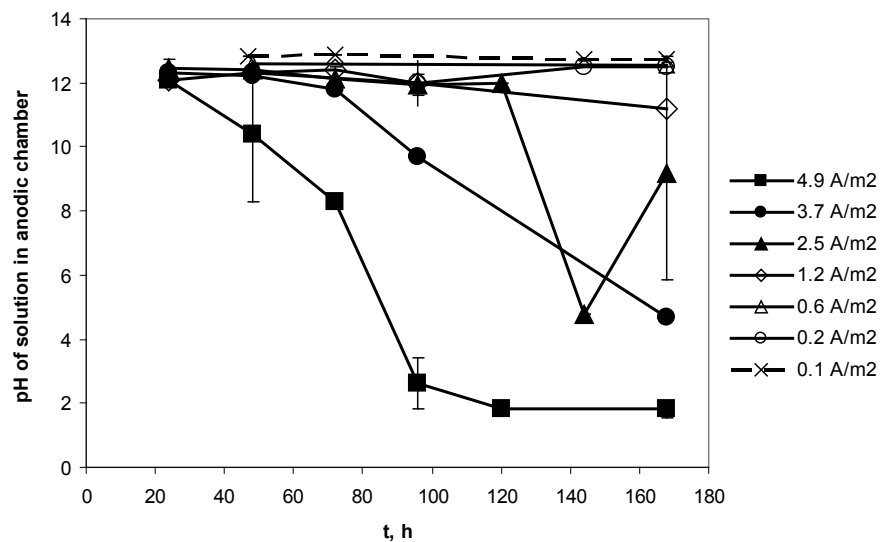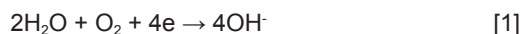Fig. 1. The experimental set-up for the electrochemical injection of corrosion inhibitor

Fig. 2. Time dependence of the solution pH in anodic chamber during electrochemical injection of the inhibitor into noncarbonated and chloride noncontaminated mortar at various current densities

3. Results

3.1. The effect of current density on the transport of nitrite ions in mortar

The composition of the solutions in both chambers changed during the tests. In the cathodic chamber, the inhibitor concentration remained practically the same, which proves that only small part of it penetrated through the membrane. However, a slight increase of pH was observed for current densities above 0.6 A/m². This change was due to reaction at the cathode:

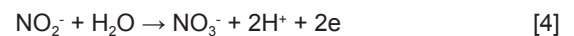$$2H_2O + O_2 + 4e \rightarrow 4OH^- \qquad [1]$$

In anodic chamber, practically no pH variations were noticed for current densities up to 0.6 A/m² (Fig. 2). Whereas, higher current densities resulted in the decrease in pH of the solution, conceivably due to the oxidation reactions occurring at the anode:

$$4OH^- \rightarrow 2H_2O + O_2 + 4e \qquad [2]$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \qquad [3]$$

This effect was intensified with increasing current density. After 7 days test at the highest applied current density (j = 4.9 A/m²), pH of

the solution in the anodic chamber dropped to value equal to 1.8. This resulted in an acid corrosion of mortar surface, which was in contact with the solution from the anodic chamber.

The concentration of the inhibitor for the solution in the anodic chamber increased gradually over time. The growth was greater, when bigger current densities were applied (Fig. 3). When the current density exceeded 1.2 A/m², nitrate ions were detected in the anodic chamber (Table 1). This means that higher current densities at the anode cause a partial oxidation of nitrite ions:

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e \qquad [4]$$

At the highest applied current densities above 80% of nitrite ions was oxidized.

The acceleration degree of the inhibitor transport was calculated as the quotient of the inhibitor concentration in the anodic chamber after 7 day tests with the application of electric field and the reference test (without electric field), respectively. Obtained values ranged from 15 up to 1900 (Table 1), and the largest gain in the acceleration degree was observed between 1.2 and 2.5 A/m². Despite the significant enhancement of the inhibitor transport at current densities above 2.5 A/m², the use of such high current densities is

not advisable due to the significant drop in the pH value and the oxidation of nitrite ions. The former effect is especially undesirable, because of the risk of acid corrosion of concrete caused by the reduced pH of the solution. The latter effect seems to be less troublesome, because the oxidation of nitrites occurs at the anode, whereas nitrite ions in the mortar membrane remain, conceivably, in unoxidized form. The anodic oxidation process is governed by the current density on the anode (in the tested system 2.5 A/m² of the surface of membrane corresponded to 0.9 A/m² of the surface of graphite electrode). Nevertheless, the increase of the applied current density above 2.5 A/m² of mortar surface is not economically justified, since the gain in the degree of acceleration is relatively small and some part of electricity is lost for undesirable reactions (oxidation of the inhibitor and production of H⁺ ions). Further experiments were carried out at a current density equal to 2.5 A/m².
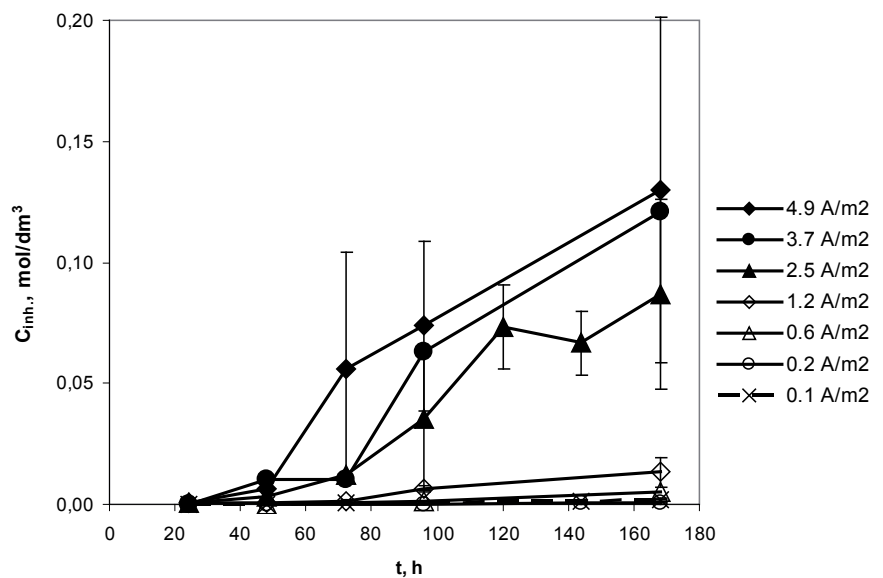

Fig. 3. Time dependence of the inhibitor concentration for the solution in anodic chamber during electrochemical injection of the inhibitor into noncarbonated and chloride noncontaminated mortar at various current densities

Table 1

RESULTS OF THE ELECTROCHEMICAL INJECTION OF THE INHIBITOR INTO NONCARBONATED AND CHLORIDE NONCONTAMINATED MORTAR (AFTER 7 DAYS)

j, A/m²	$C_{NO_2^- + NO_3^-}$, mmol/dm³	degree of acceleration	% NO_3^-	pH
0	0.068±.038	-	0	12.6±0.1
0.1	1.7±0.9	25	0	12.7±0.1
0.2	0.9±0.7	15	0	12.5±0.1
0.6	5	75	0	12.6
1.2	9±2	130	0	11.2
2.5	87±39	1300	81±14	9.2±3.3
3.7	120	1800	84	5.3
4.9	130±70	1900	83±16	1.8±0.3

3.2. Influence of the mortar quality on electric field assisted transport of nitrite ions

The rate of the inhibitor transport in concrete depends on its physical properties – primarily on the porosity and water saturation degree, and on chemical properties. In the second case, the important role played by the possibility of concrete to bind diffusing molecules by hardened cement paste components. For example, nitrite ions may be partly bound in the concrete and form salts similar to the Friedel's salt (3CaO·Al₂O₃·Ca(NO₂)₂·10H₂O) (17).

Carbonated membranes were characterized by lower absorb-

ability (Table 2), which indicates their lower porosity as compared to noncarbonated ones, because calcium carbonate, which is formed during carbonation, seals the mortar pores. Nevertheless, a faster diffusion of nitrite ions was observed in carbonated membranes (18). This phenomenon may be related to weaker binding of nitrite ions in the environment of low pH. Therefore, a faster transport of these species can be expected in carbonated membranes. The membrane porosity has a greater influence on the inhibitor migration rate (upon an impressed electric field). Therefore, lower inhibitor concentration in the anodic chamber was observed for the carbonated membranes, characterized by a lower porosity (a lower absorbability) - Fig. 4. This finding corresponds to a lesser transport acceleration of nitrite ions in the carbonated, chloride free membranes.

The addition of chlorides to the fresh mortar in case of noncarbonated membranes significantly reduces the rate of inhibitor transport. This effect can be explained by partial consumption of applied electric current for the migration of chloride ions. For carbonated membranes no significant effect of chloride ions on the inhibitor migration rate was observed. This finding is rather unexpected, because the nitrite migration should be slower in the presence of chloride ions.

Table 2

RESULTS OF THE ELECTROCHEMICAL INJECTION OF THE INHIBITOR IN MORTAR OF VARIOUS QUALITY (AFTER 7 DAYS)

Mortar membrane	Mortar absorbability, %	$C_{NO_2^- + NO_3^-}$ for 0 A/m², mmol/dm³	$C_{NO_2^- + NO_3^-}$ for 2,5 A/m², mmol/dm³	degree of acceleration	% NO_3^-	pH (anodic chamber)
noncarbonated	8.9±0.1	0.068±0.038	87±39	1300	81±14	9.2±3.3
noncarbonated with Cl⁻	9.2±0.1	0.046±0.022	12±3	250	68	11.3
carbonated	8.0±0.1	0.23±0.17	56±10	250	80±13	8.3±3.9
carbonated with Cl⁻	8.1±0.1	0.22±0.03	55±19	250	75±4	6.5±2.8

Some authors suggested that electric current passing through the mortar sample can induce the corrosion of reinforcing steel (12). Preliminary experiments were performed with steel rebars embedded in mortar membranes within this work. No corrosion damages were observed after 7 day exposure.

4. Conclusion

It was found that the use of electric field accelerates the transport of nitrite ions in mortar. The nitrite ions migration rate rises with increasing current density. However, applied current density during the electrochemical injection of the inhibitor should be relatively low (lower than 0.9 A/m^2 for the graphite anode) due to parasitic side effects in anodic chamber: a drop in pH of the solution (that causes a risk of acid corrosion of concrete) and the oxidation of nitrite ions into nitrate ions. Chloride ions present in noncarbonated membranes significantly decreased the transport rate of nitrite ions. In case of carbonated membranes the migration of nitrite ions is slower and the effect of chloride ions is slight.

As a matter of fact, the electrochemical injection of anionic inhibitors forces their migration to anode and these inhibitors are needed at the steel reinforcement. However steel rebars cannot serve as anode, because the anodic polarization can accelerate its corrosion. Therefore the practical application of the electrochemical injection of anionic inhibitors into concrete can be realized by imposing electric field between two external electrodes, located on opposites sides of rectangular structures made of reinforced concrete. These external electrodes can be settled in fibre mats, soaked with relevant solutions. Similar approach is used in field processes of electrochemical realkalization of concrete or electrochemical removal of chloride ions from concrete (19, 20). The electrochemical injection of corrosion inhibitors is feasible for elements with relatively small thickness, as building walls, decks, bridge floors, etc. This technique can be especially applicable for the conservative treatment of monumental structures made of reinforced concrete, where the use of other, generally invasive, repair methods is undesirable. The first report on the practical application of electrochemical injection of inhibitors into concrete has been just announced (21).
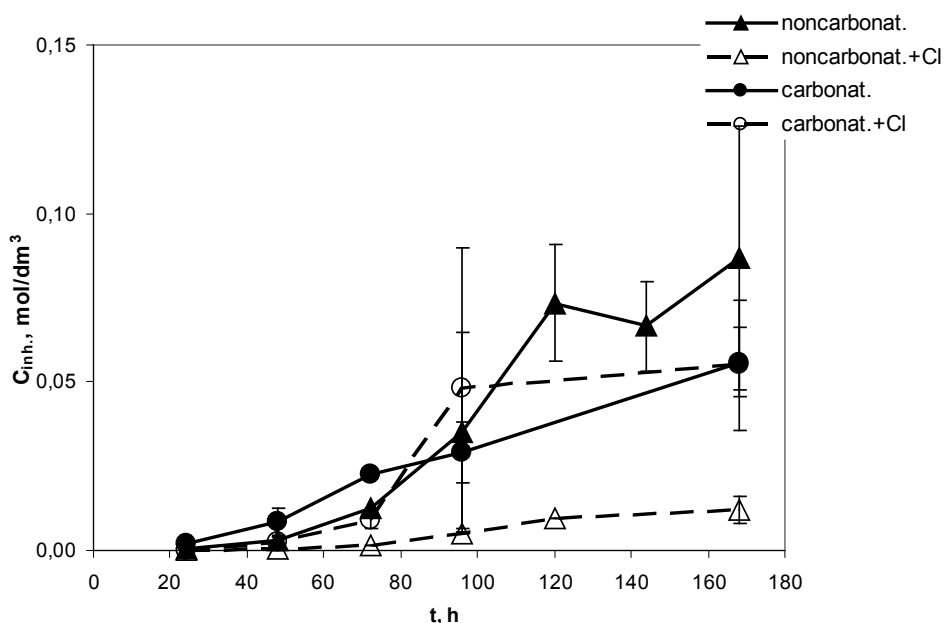
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Fig. 4. Time dependence of the inhibitor concentration for the solution in anodic chamber during electrochemical injection (j = 2.5 A/m^2) of the inhibitor in the mortar membrane of various quality

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